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Preliminary communication

A LOW-PRESSURE ROUTE TO NIOBIUM(I) AND NIOBIUM(III) CARBONYL COMPLEXES

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SUMMARY

Low pressure routes to the carbonyl complexes $[NbCl(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ and $[Nb(\eta^5-C_5H_5)Cl_2(CO)(PR_3)_2]$ (R = Me or Et) are described. Reactions involving substitution of the chloride ligand in the former are described.

The study of niobium carbonyl complexes has been hindered by the necessity to use high pressure equipment for the synthesis of either the carbonyl complexes[1,2] or the intermediates[3] used in their preparation. We now report the synthesis of representative members of two new classes of niobium carbonyl complexes by reduction of niobium halide complexes in anhydrous tetrahydrofuran (thf) by magnesium metal at 20° under one atmosphere of carbon monoxide.

Using the method of Manzer[4] we prepared the niobium(IV) complex $[NbCl_4(Me_2PCH_2CH_2PMe_2)_2]$ by reaction of $[NbCl_4(thf)_2]$ with bis(dimethylphosphino)ethane in thf. Reduction of this complex in thf by magnesium under carbon monoxide gave an orange-brown solution which after filtration and crystallisation gave the carbonyl complex $[NbCl(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ (I) in 50% yield. In some preparations a brown contaminant hindered purification; purification was readily achieved by chromatography of the crude product on a short column of Kieselgel G (nach Stahl-Merck) eluted with thf.

The complex (I) is a yellow crystalline solid, $\nu(C{\equiv}O)$ 1830, 1820, and 1760 cm^{-1} (nujol mull). The mass spectrum contained peaks at m/e 484, 456 and 428 corresponding to M^+, M^+-CO, and M^+-2(CO) respectively; the isotope splitting pattern was consistent with the presence of one chlorine atom. The ^1H n.m.r. spectrum in thf-d^8 and Me_2SO-d^6 showed a single broad resonance for the methyl and methylene protons of the phosphine at δ1.36. The tantalum analogue $[TaCl(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ reportedly[5] has a face-capped trigonal prismatic structure (Figure 1) and the Nb complex is probably similar.

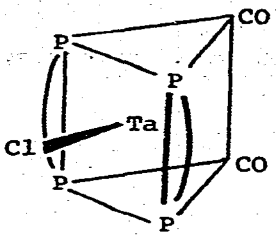

Figure 1

Complex (I) is a non-conductor in 1,2-dichloroethane. It reacts very slowly with $Na[BPh_4]$, but LiBr in thf gave a low yield of $[NbBr(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ identified by i.r. spectroscopy [ν(C≡O) 1835, 1825 and 1765 cm^{-1} (nujol mull)] and mass spectroscopy [M^+ = 529, M^+-(CO) = 501, and M^+-(2CO) = 473].

With Me_3SiN_3 in refluxing thf it gave the azido-complex $[Nb(N_3)(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ [ν(N_3) 2130 cm^{-1}, ν(C≡O) 1830, 1820 and 1765 cm^{-1}]. The analogous isothiocyanate complex could not be made using this method owing to decomposition of the silyl reagent during the reaction.

Reaction of (I) with sodium cyclopentadienide at 20° or trimethyltin cyclopentadienide in refluxing thf did not give mono-cyclopentadienyl complexes; however, mono-cyclopentadienyl niobium carbonyl complexes were synthesised using an alternative route.

Reaction of $[Nb(\eta^5-C_5H_5)Cl_4]$[6] with the basic phosphines PMe_3 and PEt_3 in thf leads to labile phosphine adducts, whose reduction with magnesium under one atmosphere of carbon monoxide gave a brown solution from which dark red carbonyl complexes were isolated by filtration and crystallisation from dichloromethane-hexane. The complexes decompose on standing in solution under dinitrogen to give a white intractible residue.

The carbonyl complex from trimethylphosphine-[Nb(η^5-C_5H_5)-Cl_2(CO)(PMe_3)$_2$](thf) has ν(C≡O) at 1940 cm^{-1}. The ^1H n.m.r. spectrum in CD_2Cl_2 has a triplet at δ4.96 $|J_{P-H}|$ = 2.6Hz, assignable to cyclopentadienyl protons coupled to two equivalent phosphorus atoms; the phosphine methyl resonances occur as a single triplet due to virtual coupling of two equivalent phosphines in a <u>trans</u>-configuration. The PEt_3 analogue [Nb(η^5-C_5H_5)Cl_2(CO)(PEt_3)$_2$] shows ν(C≡O) 1910 cm^{-1} and the ^1H n.m.r. spectrum in CD_2Cl_2 also shows a triplet due to the cyclopentadienyl protons at δ5.0; it also has complex resonances at δ1.8 and δ1.1 arising from methylene and methyl resonances respectively of the triethylphosphine. The spectroscopic and analytical data are consistent with a pseudo-octahedral arrangement of the ligands (Figure 2); detailed structural analysis of the crystalline tantalum analogue containing dimethylphenylphosphine is in progress.

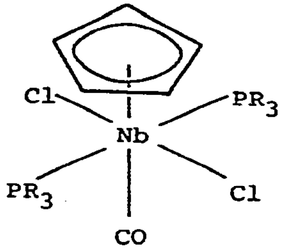

Figure 2

ACKNOWLEDGEMENT

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